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Environmental Health Center
Cincinnati, Ohio

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INDUSTRIAL WASTES RESEARCH

Environmental Health Center

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U. S. Public Health Service

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INDUSTRIAL WASTE FIELD STUDIES

Public Law 845, "Water Pollution Control Act," enacted by the 80th Congress, and approved June 30, 1948, authorizes the Public Health Service to study water pollution problems, including those associated with industrial wastes. This paper pertains to the industrial phase of this portion of the Environmental Health Center program. In this work, emphasis is placed on those industrial wastes having national or regional significance. Cooperation of industry is solicited in this work.

ORGANIZATION AND EQUIPMENT

The Industrial Wastes Section is staffed with technical personnel experienced in the subject of industrial wastes. The work is conducted in mobile laboratories which are located at the industrial plant being studied.

The field staff is a multiprofessional group requiring the services of engineers, chemists, and biologists. Each professional interest is an important and integral part of the unit. Competence is essential in the fields of sanitary, chemical, and hydraulic engineering. The chief chemist must be versed in sanitary chemistry with an aptitude for research. The role of the biologist requires specialized training in one or more of the following fields: limnology, ichthyology, aquatic entomology, algology, protozoology, and microbiology. The technical staff of the Environmental Health Center is available for consultation and occasionally specific problems are referred to the Center for research.

Two mobile laboratories are employed on each project in order to

facilitate analytical work. The units are of flexible design to permit installation of special laboratory equipment as needed for study of industrial wastes. Utilities required at the site of the mobile laboratories include: electricity, water, and sewers. Bottled gas is used for convenience. Expendable supplies are furnished from the central laboratory at Cincinnati. Engineering equipment is limited to liquid level recorders for continuously recording water levels back of weirs and in sewers.

COOPERATIVE INDUSTRIAL WASTE STUDIES

These field studies are cooperative programs with industry and with the State Stream Control Agency concerned. The primary objectives of this work are to contribute additional information on the sources and characteristics of specific process wastes, to explore potential methods for control and treatment, and to study the operations of both pilot plants and existing waste treatment systems. We collaborate with the technical staffs of industry in the examination of concentrated wastes as well as industrial effluents. This direct contact with industry is an important adjunct to review of the technical literature and is essential to full understanding of industrial waste problems.

There are a great many details to be considered in connection with these field projects, some of which take the form of comprehensive industrial waste surveys. Industrial representatives are usually from the research department but may represent any department within the company

charged with the responsibility of wastes control. Knowledge of the plant and process is a prime requisite for these technicians. The principal contributions of the industrial plant to the project include:

1. Counsel and guidance in developing the sampling program. This involves selection of sampling points, frequency of sampling, and decision as to the determinations to be made on each sample.
2. Collection of representative composite samples. Manual sampling is usually preferred for short-time studies but automatic sampling equipment may be employed when available.
3. Provision and installation of necessary facilities for accurately measuring wastes sampled.
4. Utilities for the mobile laboratories.

The Public Health Service performs the analytical work and prepares an engineering report covering the project.

These field studies are as diversified as industry itself. Efficiency of by-product recovery is occasionally determined. Evaluation of new waste treatment processes by pilot plant operation, or performance tests on full-scale equipment, are typical special studies. A solids or chemical constituent balance may be computed from test results. It is frequently possible to explain major variations of combined wastes by reference to concentrated waste data obtained from a well-organized survey. Combined treatment of industrial wastes with domestic sewage is routinely explored.

EFFECT ON RECEIVING WATERS

Surface waters must continue to receive residual liquid wastes from modern civilization. This is a recognized legitimate water use. The problem is to provide control and treatment for both domestic sewage and industrial effluents to the extent that treated wastes will not damage the receiving waters for subsequent use. Control includes prevention of waste "slugs" which may "wipe out" in a matter of hours the virtues of an otherwise well regulated system. When local conditions permit, attempt is made to correlate industrial effluents with existing conditions in the receiving stream.

There are several elements to be considered in studying a stream. Principal elements influencing stream utilization, without reference to priority, are:

1. Regimen of stream
2. Low flow frequencies
3. Assimilative capacity
4. Rates of stabilization of wastes
5. Natural pollution
6. Subsequent water use
7. Equitable distribution

PARAMETERS OF POLLUTION

Standard methods for the examination of water and sewage frequently are not well adapted to characterizing an industrial waste. Decision as to determinations to be made on a specific waste is based on water quality objectives for the stream and those parameters which best define the

pollutional characteristics of the waste. Determinations are agreed to jointly by the industrial representatives, the chemist performing the analytical work, and the engineer in charge of the field unit.

There is no universally applicable yardstick for measuring the pollutional effect of industrial wastes. Knowledge of process, of course, gives a clue as to what to expect in the waste. However, armed with all information available, the analyst is still confronted with interfering substances and the lack of sensitivity of analytical procedures. A subcommittee of Committee D19 (on Industrial Water) of the A. S. T. M. has been organized to study and develop dependable procedures for trade wastes. These analytical problems comprise a fertile field for research.

COMPLETED FIELD STUDIES

The Environmental Health Center has conducted rather comprehensive studies of process wastes from beet sugar refining, integrated steel mills, wood naval stores, and kraft pulp and paper. This work has served to define these major problems and in some instances has materially aided the industries in developing a rational pollution abatement program. A few comments pertaining to these projects will illustrate the principal field activities of the Industrial Wastes Section.

Beet Sugar Refining

Waste surveys were conducted of both straight house and Steffen processes. Pilot plant studies were made employing lime treatment of pulp

screen water and pulp press water. Fine screening of these process waters, prior to lime treatment, yielded quantities of pulp having economic significance. It was demonstrated that coagulation of pulp screen and pulp press water with 500 to 600 ppm CaO and 2 hours sedimentation could be expected to give 5-day B.O.D. reduction ranging between 30% and 47%. The treated waste was caustic and contained an appreciable residual B.O.D.

The beet sugar industry has attacked its waste problem on process level. In this instance, the philosophy of controlling pollution by process modification appears sound. Successful examples are:

1. Recirculation of flume water following screening and plain sedimentation.
2. Heating of pulp press water to 75°C. and return to the diffusion battery supply.
3. Concentration of Steffen waste in multiple-effect evaporators and incorporation of the syrup with the beet pulp thereby enhancing its nutrient value.

The most optimistic results through elimination, re-use, and by-product recovery will still leave miscellaneous wastes, bleed-off from recirculation systems, and lagoon supernatant requiring treatment except in those locations where there is adequate dilution in the receiving stream. Some natural purification is accomplished in a lagoon over a period of several months. The British Water Pollution Research Labora-

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tory has shown that settled flume water, containing about 2 per cent pulp screen and press water, was amenable to biological filtration.

Integrated Steel Mills

Cooperative waste studies were conducted at three steel mills, two of which were integrated mills producing coke, pig iron, and steel. Wastes from a total of five by-product coke plants were examined on this project. Because of the magnitude of these mills and in the interest of obtaining comparable data, each mill was divided for purpose of waste study into three principal departments, namely:

By-Product Coke

Blast Furnace

Rolling Mill

Although field work with the steel mills has been completed, the analytical results have not been cleared, with the industry, for publication. This condition limits the amount of data that can be presented at this time.

1. By-Product Coke

The by-product coke investigation disclosed several objectionable wastes, in addition to those commonly reported, and contributed substantially to knowledge of the factors which influence the characteristics of such wastes. Emphasis was placed on phenol, cyanide, and ammonia. Phenol production is known to decrease as the tar and tar acids are cracked at the higher coking temperatures. Conversely, cyanide increases as ammonia breaks down with increase in carbonization temperature. Equipment design, maintenance, and

operations are believed to be significant factors influencing the amounts of these constituents in by-product coke wastes.

Short tests were made to determine the efficiency of both the Koppers vapor recirculation and the benzol extraction processes for dephenolizing ammoniacal liquor. The benzol extraction process removes phenol from the liquor ahead of the ammonia still. Feed to the Koppers dephenolizing column (vapor recirculation) is taken from the base of the ammonia still free leg. This means, for the Koppers process, that some phenol carries over with free ammonia into the gas stream to appear later in the condensates at the by-product plant. Maximum removal of phenol by benzol extraction was 93%, representing a higher over all efficiency than that observed for the vapor recirculation process.

Ammonia still performance was investigated under various operating conditions. Operation variables explored included: rate of feed, lime dosage, and steam consumption. These studies demonstrated a relation between steam consumption and phenol carry-over. Likewise, efficiency of ammonia recovery was closely related to lime dosage. Hydrolysis of cyanide appeared to be a function of steam consumption and lime dosage.

Special studies were made of two gas final cooler systems employing Marley cooling towers for the recirculated water. This work indicated substantial amounts of cyanide and sulfide being removed from the gas and emitted to the atmosphere.

2. Blast Furnace

Dust is removed from blast furnace gas in order to reduce corrosion, to

prevent difficulties in using the gas, and to recover the dust. Approximately two thirds of the dust is removed in the dry state in devices known as "dust-catchers." The gas is further cleaned by means of wet washers followed by electrical precipitators or by disintegrators.

Liquid wastes are discharged from the wet washers and precipitators. The volume of this discharge ranges from 1500 to 5000 gallons per ton of pig iron produced. Suspended solids, which are the principal pollutional feature, range from 600 to 3500 parts per million. Efficient removal of these suspended solids is accomplished by plain sedimentation in clarifiers equipped for continuous sludge withdrawal.

3. Rolling Mill

Waste water from roll-cooling and descaling contain suspended solids, oil, grease, and soluble iron. The suspended solids are fine particles of oxide (mill scale) which are removed from the steel surface in rolling. Oil and grease enter the water system from leaks around bearings and from oil placed on products as a protective coating.

Removal of the oxide film from certain steel products is necessary prior to further processing. This is accomplished by immersion in a dilute acid bath. Liquid wastes from this operation are the intermittent discharge of spent acid and alkali solutions and the continuous water washes. In addition to the excess free acid and alkali, these wastes contain a large amount of soluble ferrous sulfate. Oil and mill scale losses, based on pounds per ton of steel product, varied appreciably depending on the type of mill.

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Wood Naval Stores

Fourteen wood naval stores plants are currently in operation in five Gulf Coast states. The principal raw materials used by these plants are the stumps from two species of southern pines, long leaf yellow and slash pine, that were left in the ground from prior lumbering operations. Rosin, turpentine, pine oil, dipentene, and other terpene chemicals are obtained from the shredded stumps by steam and solvent extraction. Furfural and gasoline are employed for special extraction.

Comprehensive industrial waste surveys were conducted at two of these naval stores plants. One of these plants used naphtha as the solvent and produced only primary products. The other plant used benzene for extraction and produced a variety of secondary products. Secondary units included facilities for hydrogenation, disproportionation, isomerization, and polymerization of the pine products, and a synthetic resin plant which used various grades of rosin to produce esters, ester gums, and synthetic resins.

Volumes and characteristics of the principal wastes from primary and secondary units as well as the total pollution loads from the plants were determined. The major liquid wastes resulting from naval stores manufacture are:

(1) Stump washer water used to clean the pine stumps prior to reduction and extraction.

(2) Drop solution water from washing the crude solution prior to refining.

(3) Solvent recovery water from low pressure evaporators of the solvent recovery system.

(4) Oil recovery water from fractional distillation of crude terpene oils.

(5) Furfuraldehyde recovery water from the solvent recovery system (resulting from the benzene extraction system only).

Secondary wastes are produced at only a few plants and are listed below:

(1) Polymerization process water from acid and solvent recovery units.

(2) Disproportionation process water consisting of condenser and wash waters.

(3) Hydrogenation process waste from rosin distillation units.

(4) Isomerization wash water from washing treated pine oil.

(5) Synthesization process water consisting of condenser and quench waters.

Results of this work revealed means for alleviating pollution by further refining, steam stripping, and substitution of other methods for disposal of concentrated wastes. Reduction or treatment of naval stores wastes has not been practiced by the industry in the past. Efforts are now being made to solve the naval stores waste problem on the process level.

Kraft Pulp and Paper

Cooperative waste studies have been made at three kraft pulp and paper mills. One of these mills produced semichemical pulp as well as kraft. The results of this work provided pertinent data on the principal wastes inside the plants as well as the total pollution load from the mills. Opportunity was afforded to study the merits of countercurrent washing of pulp. Likewise, the efficiency in recovery of chemicals was determined inasmuch as there is a direct relation between chemical loss and wastes. Data from this project are currently being analyzed. The National Council for Stream Improvement collaborated in the development of this program.

INDUSTRIAL WASTE GUIDES

Data and information obtained from these field studies, technical literature reviews, and research serve as basis for the preparation of Industrial Waste Guides for each major industrial waste. Each Guide is a concise summary statement intended to portray the present picture with respect to process wastes from the industry. There is no reference to specific industrial plants in the Guide. Characteristic features of these Guides are:

1. An abstract containing the essential features.
2. Raw materials and finished products, enumerating these items and giving quantity relationships. Wastes are commonly expressed on a production unit basis.
3. Process description including flow diagrams illustrating in diagrammatic form the industrial process steps and waste sources.
4. Sources and quantities of wastes, discussing waste producing operations and giving quantities from individual processes and plant effluents.
5. Character of wastes, presenting analytical results of individual wastes and the composite effluent, and discussing most significant characteristics of each.
6. Pollutional effects, explaining principal objections to discharge of each waste to streams and lakes.
7. Remedial measures, including: by-product recovery, elimination, segregation, reuse, and treatment of residual wastes.
8. Bibliography.

ASSISTANCE TO STREAM CONTROL AGENCIES

The industrial-waste research program of the Environmental Health Center has been set up to aid the states, interstate agencies, municipalities, and industry in the solution of industrial-waste problems. Direct assistance, in the form of professional services, has been made available to states in

the development of state programs.

Cooperative field studies serve to reduce industrial waste problems to a common denominator. Representatives of Stream Control Agencies, who collaborate in the work, develop a better understanding of industry's problems and the management of industry in turn becomes more appreciative of the need for pollution abatement. Although this work is not intended to solve industrial waste problems, the results obtained frequently contribute either directly or indirectly to solutions.

FUTURE PROGRAM

It is planned to continue the field program leading to preparation of additional industrial waste guides for those major industries not now covered. In addition, within budgetary limitations, it is proposed to devote more time to special studies which would include:

1. Evaluation of new and proposed waste treatment systems.
2. Determination of the efficacy of by-product recovery in pollution abatement.
3. Performance tests for both pilot plant and full scale treatment works.
4. Laboratory research on treatment of specific industrial wastes.

Concerted effort will be made to correlate industrial effluents studied with existing conditions in the receiving waters. Emphasis will be placed on coordination and full utilization of the professional services of sanitary engineers, chemists, and biologists.

BIOLOGICAL INVESTIGATIONS PERTAINING TO INDUSTRIAL WASTES

Effective detection, evaluation, and abatement of industrial waste pollution requires the combined efforts of a number of specialists. The biologist is a key member of this team.

The biologists of the Environmental Health Center are conducting a research program designed to determine the effects of industrial wastes on aquatic populations. Major emphasis in this study is placed on the aquatic species which have recreational or economic value. Current research projects are directed to the following objectives:

1. The devising, developing, and field testing of a rapid biological method for determining the severity and extent of stream pollution and the degree of recovery.
2. The development and testing of field methods for evaluating the effects of pollution on aquatic organisms of recreational and commercial value or those having important bearing on the provision of potable water supplies.
3. The development and standardizing of bio-assay techniques.
4. The evaluation of current information on the toxicity of industrial wastes to fishes.
5. The determination of the toxicity of various materials or mixtures of wastes to fishes by means of bio-assays.

STREAM ECOLOGY

The natural purification of organic wastes is largely a biological

process and the evaluation of the effects of pollutants on aquatic life is a biological problem. Any pollutional survey is therefore incomplete unless it includes a careful study of stream ecology. Stream surveys are, in general, of brief duration, and the time at which an investigation is made cannot always be selected. Hence a requisite for the economical use of personnel is a rapid but adequate method which can be effectively applied to most streams at any season of the year to determine the severity and extent of pollution in any given stream section. Year round field studies aimed at the development of biological techniques to serve these needs are now in progress on a number of streams in the vicinity of Cincinnati, Ohio.

The development and persistence of an aquatic population indicates an environment which continuously meets the requirements of each biological element of that population during its period of residence. Non-migratory organisms, by their presence, indicate that the aquatic environment has met their growth requirements during their life span. Accordingly year round studies are being made to determine variations in habitat conditions in each pollutional zone throughout the annual cycle as well as diurnal fluctuations of important environmental conditions. Qualitative and quantitative studies are being made of the macroinvertebrates in order to correlate stream conditions with aquatic populations. Special attention is given to unusual or extreme conditions because they constitute a limiting factor in the environment even though they may be of short duration.

This work is doing much to establish the relationship between stream environment and the resulting stream population. When such relations are well defined, it will be feasible to reverse the process in other streams and use the aquatic populations, especially those forms with a long life history, to infer the environmental conditions under which they have developed in the stream. It is this property of denoting extremes of environmental conditions which have occurred during their developmental period which makes biological indicators of such help in evaluating pollutional conditions. Care must be exercised, however, in the use of aquatic populations for indicating pollutional conditions because pollution is only one of the environmental factors affecting the life of a stream. The effects of floods, tributaries, and the character of the stream must be considered. Extreme or unfavorable environmental conditions, even though of brief duration, eliminate those forms whose tolerances have been exceeded and thus the absence of the more sensitive forms is of great importance in judging past pollutional conditions. The recovery of a stream from pollution is followed by the reappearance of the more sensitive forms and a decrease in the numbers of the tolerant species. A trained aquatic biologist can appraise pollutional conditions and stream recovery in a short time after adequate data on the relation of biotic associations to the environmental conditions under which they develop have been collected, analyzed, and evaluated. Definite information on damage to sport and commercial fishing and on other economic losses due to pollution is desirable for assisting in initiating and carrying out an abatement program.

TASTES AND ODORS

Waters are now being used as sources for domestic supply which could not be so used fifty years ago. This is due to the continued improvement of water treatment processes. Many of these waters are safe from the bacterial standpoint but they are unpalatable due to tastes and odors. Many undesirable odors in water supplies are due to micro-organisms. Studies are now in progress to determine what organisms produce undesirable odors or tastes and the environmental conditions which favor or retard their development. Biological control may be used in some areas and it is essential to know the levels or concentrations at which various nutrients cause blooms of undesirable algae and other taste and odor producing organisms. Routine screening tests are also being run with a variety of algae in an effort to find an algicide which will be effective, yet selective in its action for the species of algae it is desired to control. It is desirable to have an algicide which will control certain species without affecting the over-all productivity somewhat as 2-4 D is used to control weeds in a lawn. In the future it is hoped to carry on studies for the identification of the biologically produced materials which cause tastes and odors in order that they may be more effectively dealt with in those water treatment plants where chemical and biological control is not feasible.

TOXICITY OF INDUSTRIAL WASTES

Many industrial wastes adversely affect the production of aquatic organisms of recreational or commercial importance. Some five billion pounds of fishery products are harvested each year in the United States and

our fisheries represent an important natural resource which must be preserved or restored. The damaging or destruction of sport fishing in inland waters by pollutants is an outstanding cause of widespread complaint. Methods are needed for detecting, measuring, and evaluating the effects of various pollutants on our fisheries. Limited studies are now under way for the determination of the effects of various pollutants on fishes. It is planned to modify or devise techniques for estimating fish populations in polluted and non-polluted areas in order that the effects of pollutants may be evaluated. Definite information needed includes the miles of stream rendered fishless, the areas in which qualitative changes have occurred in the fish population, rendering them less suitable from the sportsman's viewpoint, and the extent of tainting of fish flesh.

There is great need for information on the toxicity of various industrial wastes to aquatic life, particularly fishes. Industry and the various state agencies would like to have a set of standards listing the maximum amounts of various wastes which can be released into receiving waters without being lethal to fishes.

For several reasons such a set of standards is impractical. Waters vary greatly in their ability to assimilate wastes. Materials which may not be toxic in one stream may be very toxic in another. Further, because of antagonism and synergy, materials when combined may be much more toxic or less toxic than they are in simple solutions. Thus a tabulation of the toxicity of metallic ions is of limited value because when two or more of

the metals occur together, their toxicity may be greatly altered. For example, it has been found that a mixture of copper and zinc is several times as toxic as the individual components. Further, little is known of the toxicity of many substances, even in simple solutions, and little is known of the chronic toxicity of most materials. We should know the effects of exposure to low concentrations over long periods if we are to effectively evaluate toxicities.

A comprehensive survey and evaluation of the literature on the toxicity of industrial wastes to fishes has been under way for the past three and a half years. An attempt is being made to make this coverage world wide and to evaluate all pertinent papers which have appeared since 1910. The purpose of this project is to evaluate and summarize the information which is now available, and to point out areas in which more information and research is needed. The results of this study are to be reported in a series of five papers entitled "Critical Review of Literature on the Toxicity of Industrial Wastes and their Components to Fish." Part I, "Acids, Alkalies, and Inorganic Gases", appeared in the November 1950 issue of Sewage and Industrial Wastes. The second part, "The Metals (as Salts)," will appear soon.

It is essential that methods for carrying out bioassays be uniform or standardized if they are to be effectively used in the control of industrial wastes. Work on such standardization was undertaken almost four years ago by a committee composed of representatives from industry, educational insitutions, state agencies, research organizations, the Fish and Wildlife Service, and the Public Health Service. Recommended bioassay procedures using

fish have been drawn up and published in the November 1951 issue of Sewage and Industrial Wastes. Widespread use of these procedures will enable results to be directly compared.

Bioassays are usually the best and most rapid method for determining the toxicity of industrial wastes to fishes. Indirect methods of estimating the toxicity of complex industrial wastes to aquatic life in the receiving waters, based on chemical assay of the concentrations of waste components known to be toxic, are too often unreliable.

Bioassay methods, using fish as reagents, are now in the process of development. A technique has been devised and tested for the evaluation of volatile toxicants in the presence of an oxygen demand. Research is also being carried out to fill some of the gaps in our knowledge of the toxicity of wastes by studies on synergism, cyanide wastes, and in the value of complexing agents.

Bioassays can be used in a variety of ways to assist in the control of toxic wastes. First they furnish the most direct measure of the toxicity of wastes or mixtures of wastes to the fish life in a particular receiving water. By their use it is possible in some instances to regulate waste discharge in accordance with stream flow so that lethal concentrations are not reached in a stream. This was done by a plant in Louisiana with the result that periodic fish kills were eliminated. Bioassays can also be used to determine what particular portion or portions of a process are contributing the toxic materials and thus aid in the reduction of treatment costs. They can be used to test the effectiveness of treatment methods, to indicate the

amount of treatment needed, and to demonstrate the effects of new wastes on fish life.

It is essential that all pertinent fields of knowledge be utilized for solution of a problem as large, complex, and ever changing as the safe disposal of our industrial wastes. Engineers, chemists, physicists, bacteriologists, and aquatic biologists at the Environmental Health Center are working as a team on diverse phases of the task. The aquatic biologists are at present directing their primary efforts toward the development of methods for the evaluation of the effects of pollution on aquatic life, domestic water supplies, and the detecting and measuring of toxic wastes. Studies are under way to determine organisms which cause tastes and odors and factors which encourage or control these organisms, to develop methods for determining the severity and extent of pollution, and the degree of recovery, and for measuring the effects on organisms of recreational and economic importance. Literature on the toxicity of industrial wastes is being evaluated, bioassay methods are being developed and standardized, and research carried on to determine the toxicity of complex wastes.

CHEMICAL LABORATORY RESEARCH ON INDUSTRIAL WASTE

A substantial portion of the activities of the Physics and Chemistry Section is devoted to problems related to industrial wastes. The research to be described in this section encompasses studies of inorganic and organic analytical procedures, characterization of complex organic materials in wastes and waters, methods for recovering representative samples of pollutants from waters and effluents, and the effects and persistence of wastes on the receiving stream and water supplies. Methods for the treatment of wastes or removal of constituents at the source or the water plant are also studied at the Center. The industrial waste research includes studies on the treatment and disposal of radioactive wastes and methods for evaluating such contamination in streams. The work in this field is rather specialized and will not be covered in this discussion.

ANALYTICAL STUDIES

The most common parameters used in the assay of industrial wastes are the biochemical oxygen demand test and chemical oxygen demand (oxygen consumed). This Center has been engaged in a study of the effect of various types of seeding material upon the 5-day B.O.D. These types include purely domestic sewage, sewage from a highly industrialized area, trickling filter and activated sludge plant effluents, and various river

waters. The effect of aging of the seed was also studied. Using a standardized substrate of glucose and glutamic acid it was found that the most consistent results could be obtained by using a seed which had been stored at 20°C. for 24 to 48 hours. A sufficient amount of seed must be used to give a five-day depletion of 0.5-0.6 p.p.m. in the control sample. With some industrial wastes, domestic sewage seed will not be effective in promoting biochemical oxidation. In such cases, the receiving stream below the point of discharge of the particular waste may be used to better advantage as a source of seeding material. In other cases, specialized seeds must be developed. A detailed report on this study is in preparation.

Many times industrial wastes are encountered which contain materials toxic to the organisms present in the B.O.D. test. In such cases a chemical oxygen demand test can frequently be used advantageously. The chemical oxygen demand test [1], which depends upon the oxidation of organic matter with dichromate in a 50 per cent sulfuric acid solution, is suggested for such wastes. This procedure has been checked against the various methods that have been published[2] including the standard permanganate method given in "Standard Methods." The dichromate reflux procedure referred to above has been found to give a higher percentage oxidation of most organic compounds and more precise results than other tests and it is being included in the forthcoming edition of "Standard Methods." In

those cases where industrial wastes are fairly uniform in composition from day to day, the relationship between the biochemical oxygen demand and chemical oxygen demand is fairly constant. In such cases industrial waste treatment plants may be controlled and evaluated on the basis of the chemical oxygen demand method with better results than with the slow biochemical oxygen demand test.

Before effects and persistence of constituents in industrial wastes may be studied, it is frequently necessary to develop new and more sensitive analytical methods for the determination of the particular constituent that causes the effect. Consequently, studies resulting in an improvement of the phenol determination in streams and polluted waters have been published[3,4]. A careful study of the procedures for the determination of pyridine and related compounds has also been published[5]. One of the most toxic materials to biological life is cyanide and a considerable amount of research has been carried out on methods for the determination of cyanide in low concentrations. This problem is complicated by the fact that cyanide exists in water in both simple and complex forms. A memorandum on the cyanide determination has been distributed[6], a paper on recent analytical studies is in preparation, but additional work remains to be done on this problem. The following table shows the sensitivity for lignin, pyridine, phenol

and cyanides for the methods that have been studied and improved at the Center.

Compound	Method	Sensitivity
Lignin	Folin-Denis	0.5 p.p.m.
Pyridine	Koenig-Reaction	<6 p.p.b.
Phenol	Gibbs Method	<3 p.p.b.
Phenol	4-Aminoantipyrine	<3 p.p.b.
Cyanide	Pyridine-Pyrazolone	<5 p.p.b.

The problem of determining dissolved oxygen in industrial wastes has also required additional attention. Studies on the polarographic determination of dissolved oxygen in waters containing sulfite waste liquors are almost completed. The factors which govern the oxidation of sulfite by dissolved oxygen have been investigated and it has been found that the polarogram changes with increased concentration of sulfite waste. The rate of oxidation of sulfite in the presence of oxygen varies with the pH of the substrate, e.g., lowering the pH decreases the rate of oxidation.

METHODS FOR CONCENTRATING AND EVALUATING CHARACTERISTICS OF INDUSTRIAL WASTE

A program has been undertaken at the Center to devise methods and techniques for the direct study of organic materials that may be present in polluted waters and industrial wastes. In many instances, the concentration of organic materials in water or waste effluents is so low that direct study of the aqueous solution is not feasible. Consequently, it is necessary to concentrate the organic materials contained in the water.

The first method studied depends upon the concentration of organic materials by means of active carbon. The water is passed through a small filter containing a good grade of activated carbon. The organic materials are eluted from the carbon with an organic solvent and the organic residue is recovered for study by distillation of the solvent. This technique, as first used on polluted water at the Center, has been described by Braus et al[7] and Middleton[8]. Figure 1 shows the typical arrangement of the carbon filter apparatus for concentrating materials in waters or wastes. This method has been successfully used to obtain organic materials that are present in concentrations of only a few parts per billion by passing large volumes (10,000 gallons or more) of water through the filter.

A second concentration procedure which is under study and is applicable to wastes containing 50 p.p.m. or more of extractable organic material is countercurrent liquid-liquid extraction. The apparatus shown in Figure 2 is one type that is being used in this work. The object of any apparatus of this sort is to provide a fine dispersion of the aqueous material flowing downward against an upward flow of diethyl ether, or other organic solvent, with provision for take-off of the extracted material. The apparatus can be adapted to handle from 5 to 50 gallons of waste with relative ease. Preliminary results on the use of this apparatus on industrial waste have been presented by Middleton et al[8].

There are no standard procedures that may be applied to the analysis of organic extracts from industrial waste that have been obtained by either of the above procedures. The chemist must implement known techniques and procedures with knowledge and experience to fit the situation and proceed accordingly. Braus et al[9] have described an approach to the systematic analysis of organic industrial waste. Organic extracts from the following industrial waste effluents have been studied by chemical separation methods, fractional distillation, and infrared analysis:

(1) Refinery gravity oil separator effluent

(2) Alkaline-butadiene wash water from a synthetic rubber plant

(3) Effluent from a naval stores hydrogenation plant

(4) Ammonia still wastes liquid from a coking plant

(5) The effluent from the manufacture of a synthetic explosive stabilizer

The partial resolution of the organic materials provides useful information in devising possible treatment methods for the waste, the study of taste and odor characteristics of the chemicals, toxicity studies, and other studies, in connection with stream pollution abatement.

EFFECTS AND PERSISTENCE IN STREAM WATERS

Although the potential oxygen consuming capacity of industrial wastes is usually given first consideration, one of the most important effects of industrial waste is their potential contribution to the taste and odor of water supplies. Consequently, the contribution of various wastes and constituents of wastes to taste and odor in water is being studied. The organic extract obtained from waste effluents by the two methods described is subjected to separation into acidic, basic, phenolic and neutral groups. Threshold odor determinations are made on solutions

prepared from each of these groups. The group determined to be most significant, usually the neutral compounds, may be fractionally distilled. Careful determinations of the odor producing groups in a waste and the determination of the quantities of such materials present will indicate the potential odor producing characteristics of such waste materials. Such studies have indicated that the neutral fraction of petroleum refining waste is the most significant one from the standpoint of odor.

The persistence of constituents contributing to taste and odor problems is largely determined by factors governing the biological assimilation of the waste components. Consequently, factors governing the biological assimilation of waste materials from typical industries have been studied at the Center. Persistence studies have been made on the following wastes:

(1) Phenolic type constituents derived from oil refineries and coking operations

(2) Pyridine and related compounds from coke and chemical processing industries

(3) Furfural and pentoses derived from food industries

(4) Lignin from the pulp and paper industry

(5) Cyanide from the coke and metal plating industries

(6) Neutral hydrocarbons from oil refinery effluents

The study of phenol and related compounds show that the dissimilation of such materials depends upon the type and quantities of material, the temperature of the river, and the relative pollution in the river. Ettinger et al[10,11,12,13] have published detailed results of the phenol persistence studies. In general, it may be stated that when 1 p.p.m. of phenol is added to normal river waters it takes an average of six days to remove it completely.

The studies on pyridine to be reported by Kroner et al indicated that the microflora present in streams was able to assimilate 1 p.p.m. in about six days. In contrast to this, furfural, the pentose sugars, and aldehydes are quite readily assimilated and do not present any difficult persistence problem.

One of the most difficult organic waste constituents to oxidize in a stream, either chemically or biologically, is lignin which is present in the effluent from pulp and paper manufacture. The oxidation of lignin added to various river waters was so slow that the lignin persisted for many months.

As stated earlier, cyanide is one of the most toxic materials to biological life. In a study reported by Ludzak, et al[14], it was found that in the presence of 0.5 p.p.m. of cyanide only 83 per cent of the normal B.O.D. would be obtained. It was found that organisms present in river waters having a previous history of cyanide pollution

were able to utilize cyanide more readily than were waters seeded with domestic sewage. The persistence of the neutral hydrocarbons discharged in oil refinery effluents which contribute to the taste and odor problem of water supplies is now under intensive study. Analytical problems present some difficulty in these studies but are being solved.

In conclusion, it may be stated that research in the field of industrial waste at the Center has been quite varied. It is realized that many problems exist which hinder the work of industrial waste evaluation, treatment and control that are not being studied at the present time. It is our desire to determine which problems of this kind are of the greatest importance to you. Important problems that require solution should be called to the attention of the Officer in Charge of the Center. You may be sure that careful consideration will be given to the activation of research, as far as the facilities of the Center permit, on such problems.

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